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RESEARCH PAPER

Effect of oxidation and crosslinking on functional, rheological and thermal properties of oat and apple starches

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Abstract

Oat (Oa) and apple (Ap) starches were isolated and chemically modified by oxidation with 10% NaOCl to obtain oxidized starches (OOa and OAp), followed by cross-linking with a mixture of 5.6 g of sodium tripolyphosphate and 11 g of sodium trimetaphosphate to obtain doubly modified starches (OCOa and OCAp). In the native and modified starches, the functional properties (swelling power and solubility, and freeze-thaw stability) and thermal and rheological properties (steady-state flow curves and paste formation profile) were evaluated. The swelling power of native and double modified starches varied from 57 to 86 g/g and the solubility from 0.8 to 6.0 g/100 g, these variables increased as the study temperature increased; the increment in these properties was greater in Oa compared to Ap. Oxidation followed by crosslinking increased the freeze-thaw stability in Oa and Ap starches at 30, 60, 75, and 90 °C. It also increased the Tg of OCAp and OCOa ≈ 9% compared to the native samples, respectively; while an inverse pattern was observed in apparent viscosity were this value decreased ≈ 0.8 Pa × s for Oa and ≈ 0.5 Pa × s for Ap compared to the double modified samples. All samples presented a thinning cut-type behavior (pseudoplastic), indicating structural differences. Cross-linking in oxidized starches produced a reinforcing matrix that was determined in the paste formation profile. Dual modification (oxidation-cross-linking) could be an alternative for using starches from underused botanical sources, such as apples and oats, with different functional properties and feasible applications in food systems.

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Keywords

Oxidized starch, freeze/thaw stability, swelling/solubility power, apparent viscosity

Introduction

Starch is one of the main raw materials used in the food industry since it provides various functional properties such as viscosity, texture, and stability in the foods to which it is added (Stasiak et al. 2011; Mahmood et al. 2017). Currently, the food industry is looking for "new starches" with various functionalities, so the use of alternative sources of starch from underused cereals and fruits represents a greater opportunity for the use of these resources (Piyachomkwan et al. 2002; Ashogbon and Akintayo 2014). In this sense, native starches from cereals such as oats and fruits such as apples have been little explored because they are obtained regionally or are poorly marketed (Berski et al. 2011; Zamudio-Flores et al. 2015b; Tirado-Gallegos et al. 2016). Apple starch has an amylose content between 40-48%, the granules have a spherical and semi-spherical shape with an approximate size of 7.5 μm, and show a type C diffraction pattern, so these characteristics directly impact the behavior of starch since it has been reported that apple starch shows a low tendency to retrograde; as well as lower syneresis and higher digestibility, compared to conventional starches such as potato and corn (Park and Chung 2021).

On the other hand, oat starch has an amylose content that ranges between 16-22%, with a higher lipid content (up to 1.7%), and like other cereals, oat starch granules present a pattern of type A diffraction with characteristic peaks that are representative of the presence of amylose-lipid complexes, and its granules have irregular or polygonal shapes. It has recently been reported that the presence of the amylose-lipid complex influences some functional characteristics, such as solubility and swelling power in starches (Punia et al. 2020). In general, starches are processed (cooked) to modify their viscosity properties from gelatinized starch, which is obtained after heating a suspension of granules above a characteristic temperature (known as the gelatinization temperature), which causes the loss of its crystallinity (Arocas et al. 2009). However, native starches (as obtained from the botanical source) present certain limitations due to their tendency to retrograde during cooling and freezing (Teng et al. 2013).

For this reason, native starches must be chemically modified (Karim et al. 2008; Teng et al. 2013). Chemical modification involves introducing functional groups within the starch molecule, resulting in different physicochemical and functional properties (Ashogbon and Akintayo 2014). Oxidation is a type of chemical reaction that modifies the characteristics and functional properties of biopolymers such as starch (de Moura et al. 2011). The most commonly used chemical reagents are hydrogen peroxide and sodium hypochlorite (Kuakpetoon and Wang 2008; Tolvanen et al. 2009; de Moura et al. 2011). Oxidized starch is widely used in the textile and paper industries due to its low gelatinization temperature, high solubility, and bright white color (Sánchez-Rivera et al. 2005; Manal et al. 2010; Dai et al. 2012). Cross-linking is another type of chemical modification performed to modify native starch. For this reason, various chemical cross-linking agents are used, such as sodium trimetaphosphate and tripolyphosphate, epichlorohydrin, and phosphoryl chloride (Ratnayake and Jackson 2008; Ashogbon and Akintayo 2014). Chung et al. (2008) reported that starch cross-linking can be affected by various factors, such as the starch source, the concentration and composition of the cross-linking reagent, the degree of substitution, pH, reaction time, and temperature. Some authors have argued that the type of cross-linking agent determines changes in the functional properties of the modified starch because the molecular structures of the cross-linked systems produced by the different cross-linking agents are different (Seker and Hanna 2006; Zhang et al. 2013; Ashogbon and Akintayo 2014).

Liu et al. (2014) reported that it is feasible to improve the functional properties of corn starch through cross-linking chemical modification and a dual oxidation-crosslinking modification. In a previous work, Xiao et al. (2012) compared the characteristics of cross-linked rice starches and two dual modifications of rice starches (oxidized-crosslinked and crosslinked-oxidized). These researchers reported that the levels of cross-linking and oxidation did not cause significant changes in the morphology of the starch granules and that through dual modification. It is possible to overcome the undesirable changes in the physicochemical and functional properties that native, oxidized, and cross-linked starches present individually. In this same sense, Sukhija et al. (2016) evaluated the effect of oxidation with sodium hypochlorite (NaOCl) at 2.5% active chlorine w/w, cross-linking with sodium trimetaphosphate (STMP) at 3% w/w, and the dual modifications (oxidation-crosslinking) and (cross-linking-oxidation) of elephant foot starch (*Amorphophallus paeoniifolius*) on the physicochemical, thermal, morphological, and paste-forming properties. They reported that the oxidized and doubly modified starches provided clarity in the paste, generating cracks on the surface of the granules, and that they decreased the amylose content and the paste formation profile. Sukhija et al. (2017) conducted a study to investigate the molecular properties of oxidized and cross-linked starch extracted from lotus rhizome (*Nelumbo nucifera*). The FTIR and XRD analyses confirmed the successful chemical modification. The swelling power (SP) and solubility of modified starch increase with temperature. The researchers observed that solubility was improved by oxidation and dual modification, while it was decreased by cross-linking. Other

authors have used oxidation modification, cross-linking, and dual modification (oxidation-crosslinking) to adapt degradable films' mechanical and water vapor permeability properties (Tanetrungroj and Prachayawarakorn 2018). To date, in the scientific literature, most studies on chemical modifications (single and dual) of starches have focused on botanical sources such as corn, wheat, tapioca, sago, potato, cassava, rice and banana (Yeh and Yeh 1993; Atichokudomchai et al. 2002; Wang and Wang 2003; Wattanachant et al. 2003; Karim et al. 2008; Li et al. 2008; Carmona-García et al. 2009; Zamudio-Flores et al. 2010; Carlos-Amaya et al. 2011; Kaur et al. 2012; Ačkar et al. 2014); while studies carried out with starches from under-used (or little studied) botanical sources such as oats and apples, in which dual chemical modification methods are used, are scarce. Therefore, this study aimed to evaluate the functional, thermal, and rheological properties of oxidized and oxidized-cross-linked starches (dual modification) and compare them with their respective native oat and apple starches, with which their feasibility could be diversified technological applications in food.

Materials and methods

Materials

A 20 kg batch of oat cereal (*Avena sativa* L. cv Bachíniva) was provided by "Avenas del Norte" company located in Cuauhtemoc (State of Chihuahua, Mexico). A 30 kg batch of apples (*Malus domestica* Bohr) in an immature physiological state was purchased from the local market (Cuauhtemoc City, State of Chihuahua, Mexico). All chemical reagents used for the proximal chemical analysis were of analytical grade and purchased from the supplier Sigma-Aldrich, Co. (Toluca, State of Mexico, Mexico).

Methods

Starch isolation

Native oat starch was isolated according to the method recently reported by Zamudio-Flores and Bello-Pérez (2013), while native apple starch was isolated using the method reported by Tirado-Gallegos et al. (2016).

Chemical modifications

Oxidation

The oxidation of both starches was archived using the method reported by Forssel et al. (1995) with some modifications. Briefly, 100 g of native starch was dispersed in 200 mL of distilled water. The pH was adjusted to 9.5 using a 2 M NaOH solution. Subsequently, 10 g of NaOCl was slowly added to the stirring dispersion while maintaining the pH between 9.0-9.5. It was allowed to react for 10 min after completely adding the NaOCl. One M H_2SO_4 was used to adjust the pH to 7.0, and the starch was sedimented. The settled starch was washed at least four times with distilled water and finally dried at 45 °C in a forced-air oven.

Crosslinking

The crosslinking of oxidized apple and oat starches was done following the method reported by Seib and Woo (1999) with some modifications: Fifty g of starch was mixed with 70 mL of water, 11 g of sodium trimetaphosphate, 5.6 g of sodium tripolyphosphate and 10 g of sodium sulfate. The pH was adjusted to 11.5 by adding a solution of NaOH (1M). The suspension was stirred constantly (250 rpm) and maintained at 45 °C for 3 h. Subsequently, it was neutralized to pH 7.0 by adding HCl (1 M). After this period, the suspension was dried in a forced-air oven (VWR, Scientific Products, model 1370GM-2, Cornellius, Oregon, USA) for 8 h at 50 °C, ground in a mortar, and sieved with a number 100 mesh (ASTM).

Apparent amylose content and proximal chemical analysis

The apparent amylose content of the starches was determined using the method reported by Espinosa-Solís et al. (2009). The affinities of the defatted starches to the iodine reagent were measured using an automatic potentiometer (model 702 SM Tirino, Metrohm, Herisau, Switzerland). The apparent amylose content was obtained by dividing the iodine affinity of the defatted starches by 20%. Proximate chemical analysis of native, oxidized, and oxidized-crosslinked starches was performed using official AOAC (2002) methods for the determination of moisture (method 934.01), ash (method 942.05), crude protein by micro-Kjeldhal (method 951.01), and lipids (method 920.39). All analyses were performed in quintuplicate for each starch sample.

Functional properties

Swelling power and solubility

The swelling power of the starches was determined according to the method reported by Subramanian et al. (1994) with some modifications. For 0.1 g (in dry weight) of the sample, 2 mL of distilled water was used and magnetic stirred for 4 h at different temperatures. Temperatures of 40, 50, 60, and 70 °C were used respectively. The mixture was centrifuged at 15,000 rpm for 15 min, the supernatant was decanted, and the wet starch pellet was weighed. The swelling power was defined as the ratio of the wet sediment's weight and the dry starch's initial weight. The solvent in the supernatant was evaporated in a forced air oven at 100 °C for 4 h. The solubility index was determined as the ratio of the dry supernatant's weight to the dry starch's initial weight. The analysis was performed at least in triplicate for each sample.

Freeze/thaw stability

Freezing/thawing stability was determined through the method reported by Varavinit et al. (2000). Thirty g of starch (in dry weight) was mixed with 470 g of water and gelatinized in a Brabender visco-amylograph from 30 °C

to 90 °C at a speed of 1.5 °C/min and this temperature was maintained for 15 min before cooling to 50 °C at a rate of 1.5 °C/min. Twenty-five g of gelatinized starch was added to centrifuge tubes and allowed to cool to 30 °C. The starch paste was frozen at −18 °C in an ultra-freezer (VWR Brand, WVR Scientific Products, Ohio, USA) for 24 h. All tubes were removed and thawed under various conditions. Five tubes were thawed for each condition. These conditions were: a) 30 °C in a water bath for 1 h; b) 60 °C in a water bath for 30 min, then at 30 °C for another 30 min; c) 75 °C in a water bath for 30 min and then at 30 °C for 30 min; d) 90 °C in a water bath for 30 min and then at 30 °C for 30 min. One sample from each thawing condition was centrifuged at 1,200 × *g* for 15 min. The clear liquid was decanted, and the residue was weighed. The percentage of syneresis was calculated as the ratio between the decanted liquid's weight and the paste's total weight before centrifugation, multiplied by 100. The analysis was performed at least in triplicate for each sample.

Evaluation of apparent viscosity

The apparent viscosity was determined using an AR1500ex rheometer (TA Instruments, New Castle, DE, USA), equipped with parallel stainless-steel plate geometry (θ = 60 mm), adapted with the Peltier system for temperature control at 25 °C. The plate system was covered with mineral oil to prevent water evaporation during the test. A gap of 500 µm was used between the plates, and the amount of sample used was 1.5 mL at a concentration of 5% (w/v) of total solids in distilled water. The apparent viscosity at 600 s^{-1} (η_{600}) was determined based on the increase in shear rate (γ) from 10 to 600 s^{-1} and observing the shear stress (τ). The curves were fitted using the Ostwald-de Wale rheological model, also known as the Power Law: $\tau = k\,\gamma^n$; where: τ = Shear stress (Pa), γ = Shear rate (s^{-1}), *k* = Consistency index (Pa × s^n), *n* = Flow behavior index (dimensionless) (Steffe 1992; Tecante and Doublier 1999). The analysis was performed at least in triplicate for each sample.

Paste formation profile

The paste formation profile was determined using the technique proposed by the AACC (2001), for which a starch dispersion at 10% (w/v) of total solids on a dry basis was prepared. Ten mL of the dispersion was transferred to the bowl of a Brabender Micro-Viscoamylography device (Brabender, OHG, Duisburg, Germany). The equipment was programmed to a heating-cooking-cooling cycle starting from an initial temperature of 30 °C, then it was heated to 95 °C, and this temperature was maintained for 10 min, then it was cooled to 50 °C and left at this temperature for 10 min. A heating-cooling speed of 3 °C/min and a stirring speed of 125 rpm were used throughout the cycle. The pasting temperature (Tp) was defined as the temperature at which the equipment detected an increase in viscosity. The maximum viscosity, the instability index (breakdown), and gel stability (setback) were evaluated (Jangchud et al. 2003). The analysis was performed at least in triplicate for each sample.

Determination of thermal properties

The thermal properties (characterized by the variables of initial gelatinization temperature = Ti; peak gelatinization temperature = Tg; final gelatinization temperature = Tf; and gelatinization enthalpy = ΔH) were determined using a differential scanning calorimeter (DSC) Perkin Elmer DSC 4000 (Perkin Elmer Inc., Waltman, USA). For this purpose, the method proposed by Paredes-López et al. (1994) was used. The thermal variables were obtained using Pyris® software version 11.0. Determinations were performed at least in triplicate for each sample.

Scanning electron microscopy (SEM)

A SEM analysis was performed on the samples of native, oxidized, and oxidized-crosslinked starches. A JEOL brand scanning electron microscope (model JSM5800 LV, Tokyo, Japan) was used. The operating conditions of 10 kV were used as the acceleration voltage and secondary electron signal. The samples were adhered individually to copper sample holders with double-sided graphite tape, covered with a thin film of gold to make them conductive to the electron beam, and finally introduced into the microscope chamber for observation.

Statistical analysis

The experiments were performed using a completely randomized design with a minimum sample size of 3 (n ≥ 3). An analysis of variance (ANOVA, P ≤ 0.05) was used employing the statistical program Sigma-Stat, version 2.03 (Fox et al. 1995). When significant differences were found, the Tukey test was applied (P ≤ 0.05; Walpole et al. 1999).

Results and discussion

Proximate chemical analysis and physicochemical properties

Table 1 shows the results of the proximal chemical analysis and the physicochemical properties of the native and modified starches. Moisture content varied significantly (P < 0.05) between native starch samples. Apple starch had 41% more moisture than oat starch. Oxidized apple and oat starches showed significantly higher moisture content (P < 0.05) than their native counterpart. The crosslinking modification did not significantly affect the moisture value in either apple or oat samples (P > 0.05). The moisture content of starches varies with storage humidity (Swinkels 1985; Aboubakar et al. 2008). Moreover, their moisture absorption capacity is related to their hydrophilic character (Zamudio-Flores et al. 2010). Oxidized starches are more hydrophilic than native starches, which has been reported by multiple authors (Adebowale et al. 2002; Zhang et al. 2009; Zamudio-Flores et al. 2015a). It is worth highlighting the higher content of

Table 1. Proximate chemical analysis and physicochemical properties of native oat (Oa), apple (Ap), oxidized oat (OOa), oxidized apple (OAp), oxidized-crosslinked oat (OCOa), and oxidized-crosslinked apple (OCAp) starch*.

Sample	Proximate chemical analysis (%)				Physicochemical property			
	Moisture	Lipids	Proteins	Ash	Amylose[a]	CHO[b]	COO^{-}[c]	DC[d]
Oa	3.50 ± 0.10[d]	8.00 ± 0.20[a]	6.40 ± 0.20[a]	1.60 ± 0.02[a]	27.12 ± 1.15[b]	Nd	Nd	Nd
Ap	5.98 ± 0.90[c]	0.18 ± 0.03[c]	0.15 ± 0.02[c]	0.05 ± 0.01[c]	31.56 ± 1.60[a]	Nd	Nd	Nd
OOa	6.67 ± 0.55[b]	6.35 ± 0.87[b]	4.04 ± 0.35[b]	0.98 ± 0.40[b]	23.07 ± 1.07[c]	0.08 ± 0.01[a]	0.19 ± 0.02[b]	Nd
OAp	7.51 ± 1.12[a]	0.11 ± 0.04[c]	0.13 ± 0.03[c]	0.04 ± 0.01[c]	28.67 ± 1.17[b]	0.13 ± 0.02[a]	0.27 ± 0.05[a]	Nd
OCOa	6.58 ± 0.67[b]	6.15 ± 0.90[b]	3.99 ± 0.71[b]	0.91 ± 0.51[b]	24.11 ± 0.97[c]	0.09 ± 0.02[a]	0.17 ± 0.03[b]	22.78 ± 2.90[b]
OCAp	7.60 ± 1.21[a]	0.10 ± 0.03[c]	0.11 ± 0.04[c]	0.06 ± 0.02[c]	27.77 ± 1.13[b]	0.11 ± 0.03[a]	0.25 ± 0.06[a]	27.60 ± 1.77[a]

*Mean of five repetitions ± standard error. Values with the same letter in each column are not significantly different ($P > 0.05$). [a]Apparent amylose content (%); [b]CHO = Content of carbonyl groups (%); [c]COO^{-} = Content of carboxyl groups (%). [d]DC = Degree of cross-linking (%). Nd = Not determined.

lipids and proteins quantified in the Oa sample (8.00% and 6.40%, respectively) compared to Ap (0.18% in lipids and 0.15% in proteins). This indicates higher hydrophobic components (lipids) in Oa compared to Ap, which could explain the higher moisture content in the Ap sample. These results are consistent with the values recently reported in oat and apple starches from varieties like those used in our study (Zamudio-Flores et al. 2015b;Tirado-Gallegos et al. 2016). Interestingly, a relatively higher amount of ash was also observed in sample Oa compared to Ap (Table 1). These variations in the proximal content of starches depend on several factors, among which are the botanical source, the variety, the agronomic conditions, the type of soil where they were grown, and the fertilization and irrigation conditions (Martínez et al. 2010; Zamudio-Flores et al. 2015b). When native starches were subjected to the oxidation treatment, a significant decrease ($P < 0.05$) in amylose content was observed (Table 1). These values decreased from ≈ 27% (Oa) to ≈ 23% (OOa), and from ≈ 32% (Ap) to ≈ 29% (OAp), without the modification by crosslinking significantly affecting these values. The decreases in amylose content may be because oxidation causes de-polymerization of amylose molecules, which would also affect their functional properties (Wang and Wang 2003; Tian et al. 2004; Li et al. 2010; de Moura et al. 2011; Argüello-García et al. 2014). No significant differences ($P > 0.05$) were observed in the content of carbonyl groups (CHO^{-}) between the different samples; however, the content of carboxyl groups (COO^{-}) was higher in OAp compared to OOa, without crosslinking modification affecting these contents. These results indicated a greater susceptibility to oxidation in native apple starch since the content of carboxyl groups was higher in this sample. This behavior may be related to more amorphous zones in apple starch than in oat starch. Although the percentage of crystallinity of apple and oat starch granules was not evaluated in this study, it has been reported in the scientific literature that oxidation mainly attacks the amorphous zones of the starch granules to a greater degree than the crystalline zones, for example, it is inferred that starches with a larger amorphous zone may present a greater susceptibility to oxidation (Kuakpetoon and Wang 2008; Pietrzyk et al. 2018a, b; Zhou et al. 2016). Finally, significant differences ($P < 0.05$) were observed in the degree of crosslinking between the OCAp sample (≈ 28%) and OCOa (≈ 23%). This corroborates the greater susceptibility to chemical modification of the Ap sample in relation to Oa, possibly due to the greater presence of amorphous zones (Vanier et al. 2012; Pietrzyk et al. 2018a, b). It has been reported that crosslinking can prevent starch component molecules (amylose and amylopectin) from rearranging during drying, which provides an exposed internal structure whereby oxidizing agents can reach the interior of the starch (Liu et al. 2014; Dang et al. 2018).

Thermal analysis

Significant differences ($P < 0.05$) were observed in the thermal variables (T_i, T_g, T_f, and ΔH) between native apple starch (Ap) and native oat starch (Oa) (Table 2). Oat's thermal variables were similar to those reported for this oat variety by Zamudio-Flores et al. (2015b) (T_i = 55.20 ± 1.12 °C; T_g = 59.65 ± 1.10 °C; T_f = 64.20 ± 1.15 °C; ΔH = 7.65 ± 1.10 J/g); however, the results of the Ap sample vary slightly with those reported in the scientific literature. For example, Tirado-Gallegos et al. (2016) found that starches isolated from apples harvested at later ripening stages had higher thermal variables. These researchers suggested that cultivar type and

Table 2. Thermal variables obtained by differential scanning calorimetry of native starches of oat (Oa), apple (Ap), oxidized oat (OOa), oxidized apple (OAp), oxidized-crosslinked oat (OCOa), and oxidized-crosslinked apple (OCAp) starches*.

Sample	Thermal variables			
	T_i	T_g	T_f	ΔH (J/g)
Oa	54.80 ± 0.90[d]	58.31 ± 0.83[d]	63.12 ± 0.87[d]	7.81 ± 0.65[c]
Ap	58.11 ± 0.29[c]	60.18 ± 0.63[c]	65.10 ± 0.77[c]	9.87 ± 0.93[b]
OOa	51.20 ± 0.60[f]	54.31 ± 0.83[f]	58.17 ± 0.87[f]	6.37 ± 0.71[c]
OAp	50.31 ± 0.33[e]	56.68 ± 0.57[e]	60.47 ± 0.77[e]	7.42 ± 0.63[c]
OCOa	62.94 ± 0.77[b]	67.45 ± 0.53[b]	72.18 ± 0.85[b]	10.35 ± 0.81[a]
OCAp	64.36 ± 0.66[a]	69.78 ± 0.75[a]	75.25 ± 0.91[a]	11.43 ± 0.90[a]

*Mean of three repetitions ± standard error. Values with the same letter in each column are not significantly different ($P > 0.05$). Ti = initial gelatinization temperature; Tg = gelatinization temperature; Tf = final gelatinization temperature; ΔH = enthalpy of gelatinization.

agro-climatic conditions affect the thermal variables of apple starches. The oxidation of native apple and oat starches, as detailed in Table 2, consistently decreased all thermal variables. This decrease can be attributed to the potential de-polymerization of the starch's amorphous regions and the formation of functional groups (CHO—and COO—). This allows greater hydration and swelling of the starch granules (Wang and Wang 2003; Sangseethong et al. 2010; Bustillos-Rodríguez et al. 2019). Oxidized starches are recommended for use in frozen foods because they improve the frozen storage stability of starch (Chung et al. 2008). Table 2 shows that double-modified starches have increased thermal variables compared to native and oxidized starches. Crosslinking modification of oxidized starches strengthens the bond between starch chains, increasing their resistance to gelatinization. This slightly increases the thermal variables associated with this process (Carmona-García et al. 2009; Ashogbon and Akintayo 2014; Park et al. 2018). Crosslinked starches are commonly used in baked goods due to their high resistance to oven temperature.

Rheological properties

Table 3 shows the rheological properties analyzed using the consistency index (*k*) and flow behavior index (*n*) variables evaluated with the application of the Power Law model, in addition to the apparent viscosity obtained at 600 s^{-1} (η_{600}) and the coefficient of determination (R^2). The chemical treatment by oxidation significantly decreased ($P < 0.05$) the rheological variable of η_{600}. Regarding the variable *k* in the oat starch sample, a decrease in the numerical value was observed, although this decrease was not statistically significant ($P > 0.05$), so it can be stated that oxidation had no impact on this variable. However, a different behavior was observed in apple starch since the treatment caused a significant decrease in the value of *k*. The rheological variable *n* increased due to the oxidation treatment since it caused an increase in both samples compared to the value of the native starches. The values presented in the variable *n* indicate a predominance towards non-Newtonian type behavior, known as shear-thinning (pseudoplastic), and is characterized by presenting values less than 1 ($n < 1$) (Pepe et al. 2015; Tirado-Gallegos et al. 2016). The shear-thinning behavior is attributed to a lower rate of re-formation in the biopolymer structure as the shear rate increases (Salamone 1996; Shah et al. 2017). On the other hand, some studies have reported the relationship between amylose content (%Am) and apparent viscosity (η_{ap}) concerning the applied shear speed. Utrilla-Coello et al. (2013) evaluated the rheological properties of starches from different banana varieties. They reported that Valery variety banana starch showed a low %Am and η_{ap} content compared to the other botanical sources analyzed. These authors suggest that %Am plays an important role in decreasing η_{ap}. At the same time, Xie et al. (2009) reported a positive linear relationship between %Am and the flow behavior index (*n*, which is considered as the exponent obtained through the power law). In this sense, it was observed that oat starch presented the lowest values of both %Am and *n* and that apple starch presented an inverse behavior. Similar results were reported by Utrilla-Coello et al. (2014), who evaluated the physicochemical, thermal and rheological properties of starches isolated from different banana cultivars, visualizing that the value of *n* was lower in the cultivars with a lower %Am, which they attributed to the mechanism of breakdown of the structure of the starch network during shear or shear stress (since the breaking speed was greater than the rearrangement of starch molecules at higher shear rates). Consequently, this impacts the decrease in apparent viscosity because this elastic characteristic is mainly provided by %Am (Xie et al. 2009).

Table 3. Rheological variables of the consistency index (*k*), flow behavior index (*n*), apparent viscosity (η_{600}) evaluated at 600 s^{-1} and coefficient of determination (R^2) of the Power Law model in native oat (Oa), native apple (Ap), oxidized oat (OOa), oxidized apple (OAp), oxidized-crosslinked oats (OCOa) and oxidized-crosslinked apple (OCAp) starches*.

Sample	Rheological variables			
	η_{600} (Pa × s)	*k* (Pa × s^n)	*n* (dimensionless)	R^2
Oa	2.25 ± 0.50^{a}	11.20 ± 0.20^{c}	0.78 ± 0.01^{c}	0.985
Ap	1.50 ± 0.10^{b}	18.50 ± 0.15^{b}	0.65 ± 0.12^{d}	0.981
OOa	0.90 ± 0.20^{d}	9.25 ± 0.11^{c}	0.91 ± 0.15^{b}	0.991
OAp	1.05 ± 0.13^{c}	7.15 ± 0.35^{d}	0.95 ± 0.10^{a}	0.990
OCOa	1.41 ± 0.27^{b}	20.45 ± 0.21^{a}	0.96 ± 0.11^{a}	0.981
OCAp	0.95 ± 0.47^{d}	20.20 ± 0.15^{a}	0.96 ± 0.08^{a}	0.987

*Mean of five repetitions ± standard error. Values with the same letter in each column are not significantly different ($P > 0.05$).

Pasting properties

Significant statistical differences ($P < 0.05$) were observed in the paste formation profile between native oat and apple starches (Table 4). In general, apple starch presented a higher viscosity during the paste formation profile, and according to the visco-amylographic variables, it was observed that the oat starch sample presented a lower viscosity peak than the apple starch. A higher peak viscosity reflects the ease of the granules to swell freely before breaking (Tecante and Doublier 1999). In all samples, it was observed that the viscosity increased during the cooling stage due to the reorganization of the linear chains, which leached out during the heating stages, and a greater number of union zones during the formation of the paste and, therefore, the establishment of a network that retained a greater amount of water (Casarrubias-Castillo et al. 2012). This behavior may be related to the internal organization of the granules since, according to the X-ray diffraction pattern, type

Table 4. Visco-amylographic variables (paste formation profile) of starches from oat (Oa), apple (Ap), oxidized oat (OOa), oxidized apple (OAp), oxidized-crosslinked oat (OCOa), and oxidized-crosslinked apple (OCAp)*.

Sample	Visco-amylographic variables							
	T_{emp} (°C)	PV (UB)	$V_{95\,°C}$ (UB)	V_{ienf} (UB)	V_{fenf} (UB)	$V_{set\text{-}back}$ (UB)	Stability ($PV\text{-}V_{ienf}$)	Gelatinization index ($V_{fenf}\text{-}V_{ienf}$) (UB)
Oa	79.0 ± 1.2^{c}	248.5 ± 9.5^{d}	170.8 ± 4.5^{e}	247.8 ± 1.6^{e}	710.5 ± 2.7^{c}	471.5 ± 5.1^{a}	0.7 ± 0.1^{f}	462.7 ± 8.6^{a}
Ap	79.1 ± 2.1^{c}	270.6 ± 5.8^{b}	193.6 ± 5.7^{c}	260.1 ± 2.8^{d}	725.4 ± 3.9^{a}	378.8 ± 4.1^{f}	10.5 ± 0.3^{a}	465.3 ± 9.5^{a}
OOa	77.2 ± 0.9^{d}	260.1 ± 6.9^{c}	187.2 ± 3.1^{d}	253.5 ± 3.6^{c}	717.8 ± 2.1^{b}	441.6 ± 3.6^{c}	6.6 ± 0.7^{c}	464.3 ± 6.8^{a}
OAp	80.5 ± 1.1^{b}	280.8 ± 3.7^{a}	205.8 ± 4.9^{a}	$272.3 \pm 2.1^{a,b}$	689.6 ± 5.1^{d}	450.4 ± 3.8^{b}	8.5 ± 0.8^{b}	417.3 ± 7.4^{b}
OCOa	82.1 ± 1.8^{a}	275.1 ± 5.1^{a}	198.1 ± 2.3^{b}	270.6 ± 1.7^{b}	670.3 ± 2.8^{e}	435.8 ± 2.8^{d}	4.5 ± 0.3^{e}	399.7 ± 9.2^{c}
OCAp	79.2 ± 1.0^{c}	278.5 ± 7.8^{a}	$200.3 \pm 1.8^{a,b}$	$272.6 \pm 1.9^{a,b}$	690.7 ± 3.5^{d}	422.4 ± 3.5^{e}	5.9 ± 0.6^{d}	418.1 ± 8.1^{b}

*Mean of five repetitions ± standard error. Values with the same letter in each column are not significantly different ($P > 0.05$).

C starches have an open structure, which gives them the possibility of hydrating (causing swelling) in greater proportion. In contrast, the structure of cereal starches such as oats is mostly closed, which limits their swelling; in addition to the presence of the amylose-lipid complex, which reduces the swelling capacity (Wang and White 1994; Galdeano et al. 2009; Punia et al. 2020). On the other hand, oxidation increased the viscosity in both starch sources compared to their respective native counterparts. This was because the oxidation modification was carried out in the amorphous areas of the starch, causing a greater incorporation of water molecules and, therefore, an increase in the swelling of the starch granules and, consequently, in viscosity. These results agree with the findings observed in the thermal properties; however, some authors have reported a behavior contrary to that observed in this study in relation to oxidized starches obtained from other botanical sources such as potato, corn, rice, barley (Kuakpetuoon and Wang 2012; Spier et al. 2013; Halal et al. 2015) and lotus root (Sukhija et al. 2017). It has been reported that the decrease in viscosity is due to a weakening of glycosidic bonds caused by oxidation, leading to a reduction in the molecular weight of starch components (Sukhija et al. 2016).

Scanning electron microscopy (SEM)

SEM results indicated differences in the morphology and size of oat and apple starch granules (Figs 3, 4). The oat starch granules presented mostly irregular shapes, while apple starches adopted round, spherical, and dome shapes. These results are consistent with other studies in which similar shapes were reported in starch granules of oat cereal varieties Bachiniva, Cuauhtemoc, and Teporaca (Zamudio-Flores et al. 2015b) and in relation to the morphology of apple starches, Tirado-Gallegos et al. (2016) reported the geometric shapes (round and spherical) in apple starches from the Golden Delicious Smoothee variety. Several researchers have observed that the morphology and size of starch granules are mainly dependent on the botanical source from which they are obtained (Agama-Acevedo et al. 2015; Méndez-Montealvo et al. 2015; Tirado-Gallegos et al. 2016).

Functional properties

Swelling power and solubility

The swelling beginning indicates the granules' water absorption rate during heating (Muñoz et al. 2015). The swelling power and solubility increased by increasing the evaluation temperature from 40 to 70 °C (Fig. 1). Various researchers have previously described this behavior; for example, Wojciechowski et al. (2018) evaluated the physicochemical, structural, and thermal properties of common bean starch (*Phaseolus vulgaris* L.) subjected to oxidation, acetylation, and dual modification treatments (oxidation-acetylation). They observed that the swelling power and solubility increased in both starches (native and modified) as a consequence of the gelatinization phenomenon, which can begin at low temperatures (≈ 50 °C) and the leaching of amylose (at higher temperatures), this behavior being mostly evident in oxidized starch (Halal et al. 2015; Wojeicchowski et al. 2018). Concerning other botanical sources, studies are limited in terms of the evaluation of certain functional properties.

Freeze/thaw stability

The assessment of how well foods tolerate being frozen and thawed is an important factor in determining their quality. This property is particularly relevant for foods that are stored in refrigeration, as it indicates the amount of water that they may lose over time. According to Charoenrein et al. (2008), this process is called syneresis. Fig. 2 displays the outcomes of the freeze-thaw stability tests performed on both native and modified apple and oat starches. Samples were stable at 30, 60, and 90 °C, but behaved differently at 75 °C. Syneresis (%) increased with the number of cycles, consistent with Zamudio-Flores et al. (2015b) in oat starches of different varieties subjected to freeze-thaw cycles at temperatures ranging from 30 to 90 °C.

These authors inferred that starch retrogradation caused water expulsion from the gel during the freezing and thawing process, due to increased molecular associations between polymer chains within the starch structure. Higher levels of syneresis were observed in the double-modified starches (OCAp and OCOa), followed by the oxidized starches (OOa and OAp) and the native starches (Oa and Ap). In addition, native, oxidized, and oxidized-crosslinked modified apple starches presented greater syneresis than oat starches. There is ongoing debate

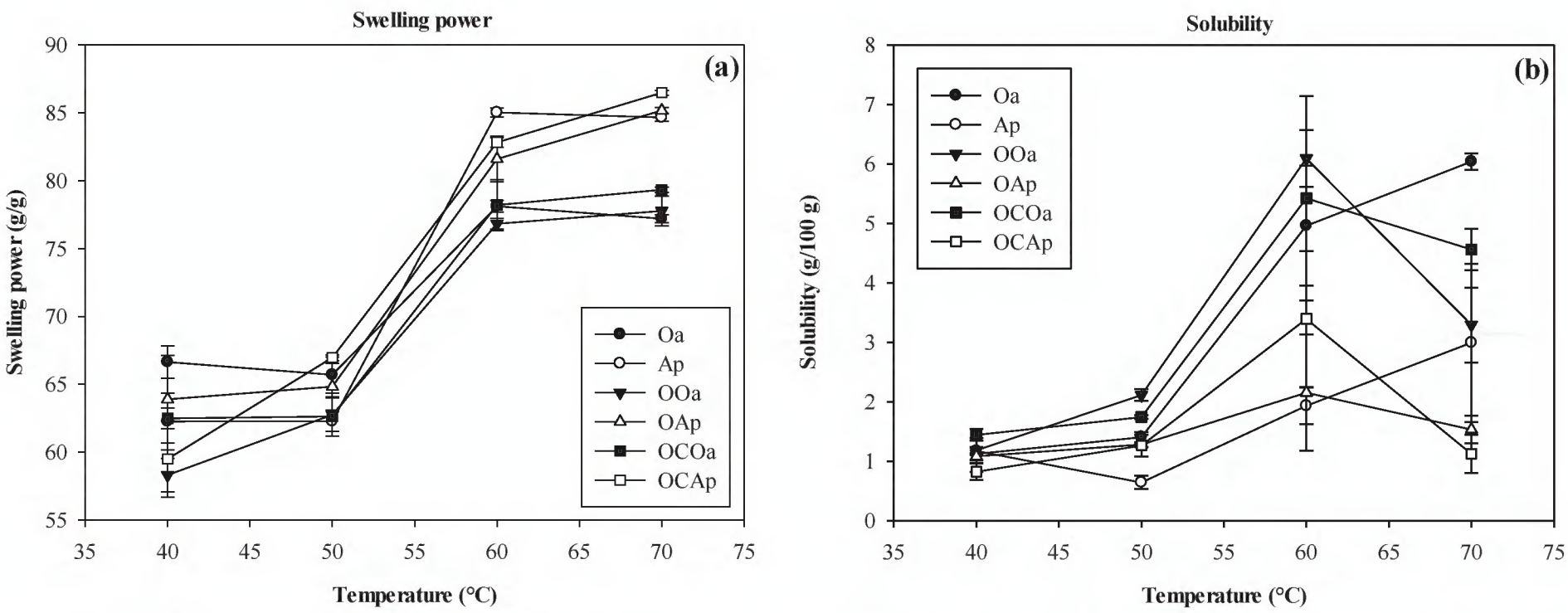

Figure 1. Swelling power (**a**) and solubility (**b**) of native and modified starches. Mean of three repetitions ± standard error bars.

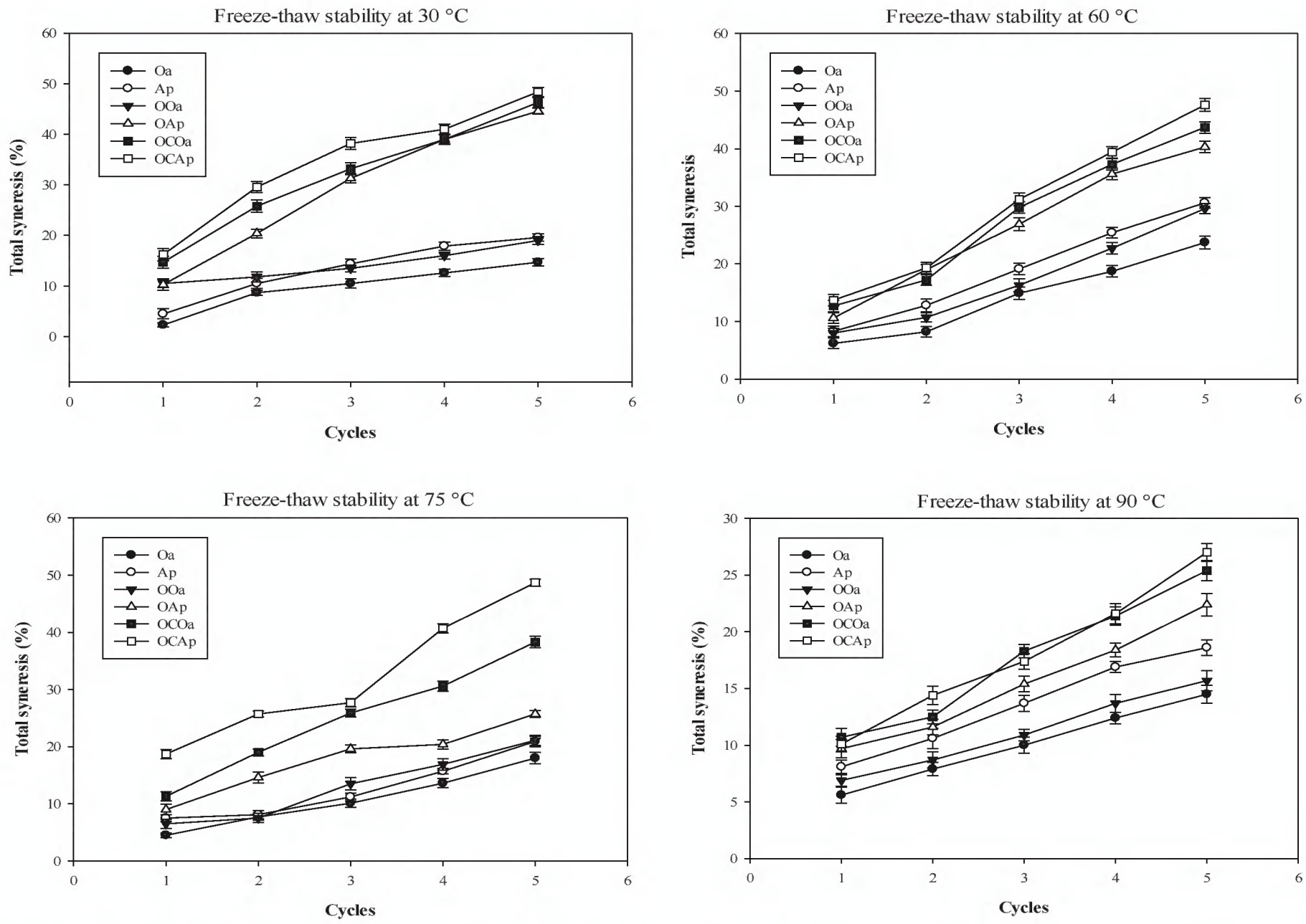

Figure 2. Freeze-thaw stability of native and modified starches. Mean of three repetitions ± standard error bars.

surrounding the efficacy of modified and double-modified starches with respect to their functional properties, according to the literature. For instance, our findings are similar to those reported by Bello-Pérez et al. (2002). The researchers observed that modified corn starch, which underwent acetylation with acetic anhydride and alcoholic-alkaline treatment, had lower freeze-thaw stability than its native counterpart in all study cycles. However, modified banana starch (*Musa paradisiaca* L.) exhibited greater freeze-thaw stability. These researchers indicated that modifying banana starch can improve the stability of frozen foods. By generating a more linear structure, the chains gradually aggregate and form a three-dimensional mesh, reducing the amount of water removed during the freezing and thawing process. However, not all modified starches behave the same way in terms of freeze/thaw stability. The results agree with Liu et al. (2014), who explored the effects of oxidizing and cross-linking corn starches with hydrogen peroxide and sodium trimetaphosphate. The modified starches had lower freeze-thaw stability than the native starches, likely due to higher oxidation levels interfering with gel system formation after freezing.

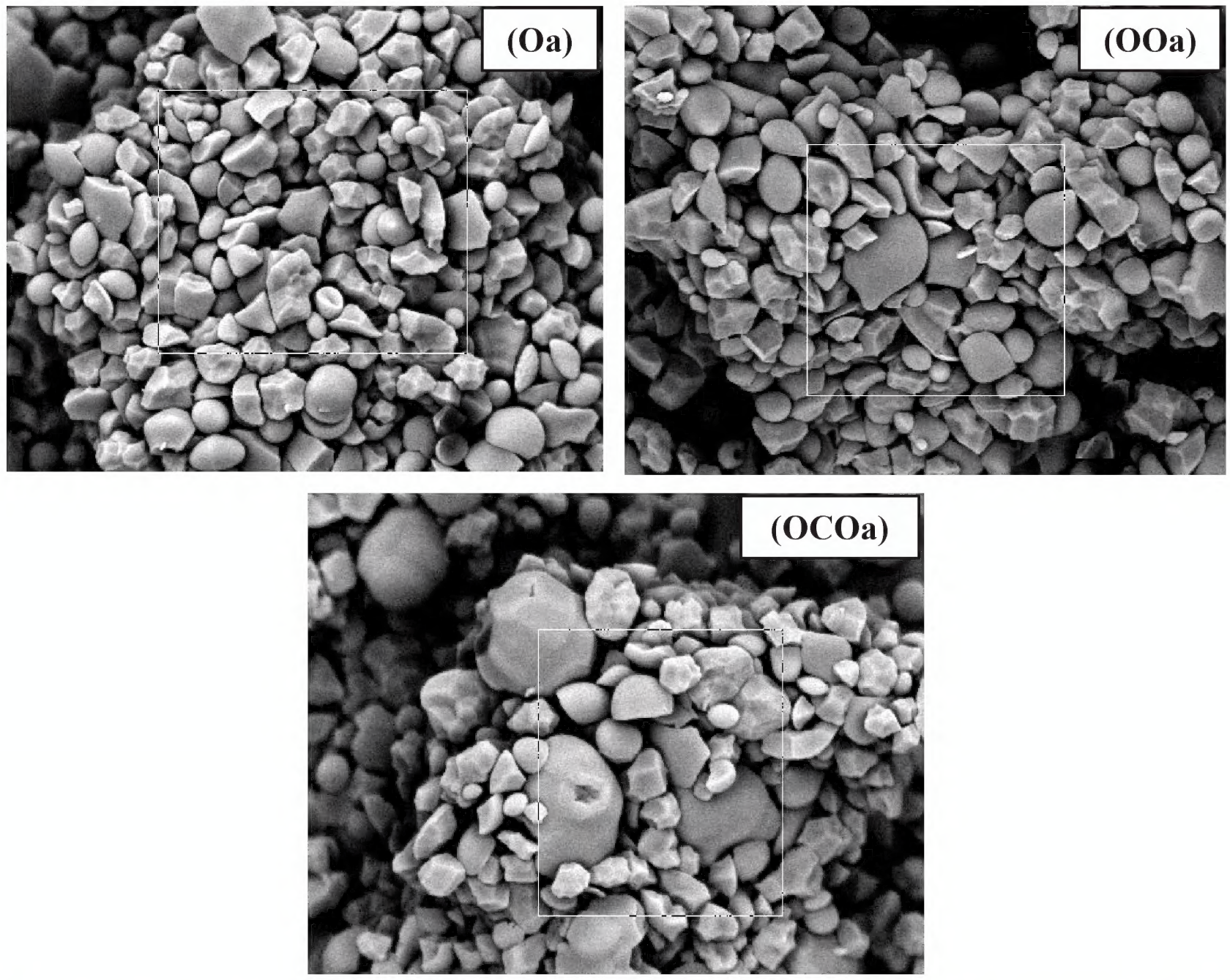

Figure 3. Scanning electron micrographs of native oat starch (Oa), oxidized oat starch (OOa), and oxidized-crosslinked oat starch (OCOa).

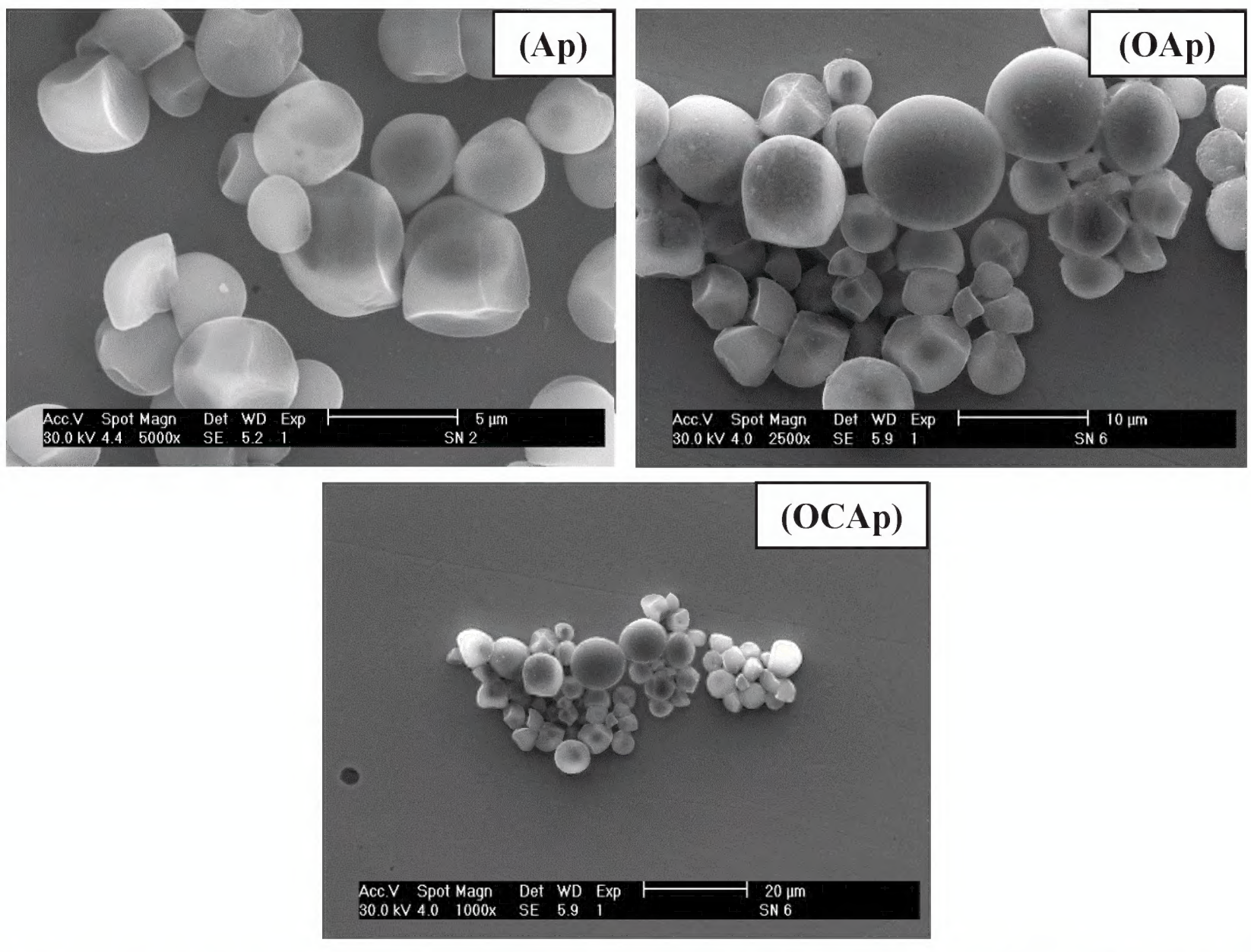
(Ap)
Acc.V Spot Magn Det WD Exp 5 µm
30.0 kV 4.4 5000x SE 5.2 1 SN 2
(OAp)
Acc.V Spot Magn Det WD Exp 10 µm
30.0 kV 4.0 2500x SE 5.9 1 SN 6
(OCAp)
Acc.V Spot Magn Det WD Exp 20 µm
30.0 kV 4.0 1000x SE 5.9 1 SN 6

Figure 4. Scanning electron micrographs of native apple starch (Ap), oxidized apple starch (OAp), and oxidized-crosslinked apple starch (OCAp).

Conclusions

The chemical modification by oxidation was carried out mainly in the amorphous regions of both botanical starch sources. Oxidation and oxidation-crosslinking significantly changed the thermal, functional, and rheological properties of native oat and apple starches. The dual modification of apple starch presented greater syneresis at all temperatures studied and showed greater thermal stability. The results suggest that these starches could be used in the food industry, specifically in preparing sauces or food dressings, since these starches could increase the viscosity of sauce, giving it a smoother and more appealing texture, and the starch particles hydrate and swell when mixed with water, forming a thick gel-like consistency.

Conflict of interest

There are no conflicts of interest.

Author´s contributions

J.P. Sida-Arreola: Writing original draft, review and editing, methodology. J.P. Zamudio-Flores (the corresponding author) designed the research plan, execution of experimental work, interpretation of results and conceptualization. V. Espinosa-Solis contributed to the writing of the manuscript and designed the Figures. R. Calderón-Díaz, G. Vela-Gutiérrez, G. Pacheco-Vargas, A.I. Saenz-Mendoza and M.P. Castro-Mendoza participated in the experimental design and methodology. M. Hernández-Gonzaléz, H.Y. López-De la Peña and A. Ortega-Ortega performed some analysis and contributed in the translation of the manuscript.

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